Chapter

Recent Progress in the Electrochemical Exfoliation of Colloidal Graphene: A Review

Randhir Singh

Abstract

Graphene is a wonder nanomaterial which is used in a wide variety of electronics applications because of its excellent electrical, optical, chemical and mechanical properties. For the efficient use of graphene in the preparation of modern electronics devices it is imperative to first prepare a colloidal solution of graphene. Although various techniques are being used for the synthesis of colloidal form of graphene, the synthesis of colloidal graphene via electrochemical exfoliation is time saving and easy, facile method which can be easily performed in the laboratory without any expensive and sophisticated equipment as required in other techniques. Through electrochemical exfoliation of colloidal graphene, high quality graphene can be obtained within short time. Further, after the electrochemical exfoliation of colloidal graphene, the colloidal solution is stable in the organic solvent for few weeks. The conducting electrodes prepared by this colloidal solution of graphene have wide application in the areas of flexible energy storage devices and sensors fabrication.

Keywords: colloids: graphene synthesis, electrochemical exfoliation, energy storage device

1. Introduction

Graphene is the wonder nanomaterial discovered in 2004, most widely investigated because of its excellent electrical, mechanical, optical, chemical properties [1, 2]. The main properties are it is 97.7% transparent and is used for making transparent conducting electrodes. Its high carrier mobility (200,000 $cm^2 v^{-1} s^{-1}$), Young's modulus of 1.0 TPa is another important properties of graphene. It is considered 200 times more conductive than copper and 100 times stronger than steel [3–7]. In addition to this it is very flexible in nature as it can be stretched to 20% of its original length. These exceptional properties of graphene are highly suitable for the fabrication of various modern electronics device applications such as energy storage devices and sensors etc. However, for the efficient use of graphene in these modern devices, the colloidal dispersion of graphene has to be prepared for using in solution phase. The colloidal solution of graphene has some advantages in comparison to the other forms of graphene to be utilized for the formation of various devices.

Nowadays the modern electronics devices are being fabricated using printable electronics process. For the fabrication of the electronics devices such as sensors, energy storage devices using printable electronics the graphene has to be available in the colloidal solution form so that it will be easy to fabricate these graphene based flexible electronics devices using spray coating, brush coating, screen printing techniques [8]. Therefore, it is absolutely necessary to produce the colloidal solution of graphene.

2. Limitations of graphene synthesis methods

Various methods have been used for the preparation of graphene each having its own limitations as compared to others. Some of the prominent methods are mechanical exfoliation, Hummer's method, liquid phase exfoliation, epitaxial growth, chemical vapor deposition etc. First, the mechanical exfoliation method by which the graphene was first exfoliated from solid graphite source is a very time consuming technique of producing graphene from graphite [1]. It is a hit and trial method in which the researcher is not sure whether the graphene exfoliated on the scotch tape is single layered or multi layered graphene sheet. So, it is not a controllable and leads to a lot of wastage of time. Similarly the hummer's method uses very harmful acids and is also very time consuming method. The quality of graphene obtained from this method is not of high quality as indicated from the TEM results of graphene sheets.

Chemical vapor deposition requires very expensive and sophisticated equipment, hence the synthesis cannot be performed in all the laboratories [9, 10]. Liquid phase exfoliation is a technique where long hours of sonication process is required which is very time consuming process [11]. Further the long hours of sonication deteriorates the quality and size of graphene nanosheets in the dispersion. Therefore, among other methods of graphene synthesis it is found that the colloidal dispersion of graphene prepared by electrochemical exfoliation is time saving method, economical and easy to use in any laboratory without any sophisticated and expensive equipment. The relative advantages of electrochemical exfoliation method in comparison to others methods is shown in **Table 1**.

S.No.	Graphene synthesis method	Relative advantage/disadvantage
1	Liquid phase exfoliation	Requires Long hours of sonication, Time consuming
2	Epitaxial growth	Low yield, Difficult in graphene layer transfer
3	Chemical vapor deposition	Requires expensive and sophisticated equipment
4	Mechanical exfoliation	Not suitable for large scale production of graphene
5	Hummer's method	Harmful chemicals, acids used, graphene not pure
6	Electrochemical exfoliation	FASTER, HIGH YIELD, ENVIRONMENT FRIENDLY

Table 1.
Relative advantages of electrochemical exfoliation method in comparison to others.

3. Colloidal graphene

A colloidal solution of graphene (**Figure 1**) has graphene nanoparticles evenly distributed throughout the solution. In the colloidal solution of graphene the graphene nanoparticles remain dispersed in the solution without settling to the bottom, for quite a long time. Further, The colloidal solution of graphene has very large surface area and exhibits high electrochemical behavior. Further, the advantage of using solution phase to form various graphene devices such as sensors, electrodes, energy storage devices makes it more prominent method as compared

Figure 1.
Colloidal solution of graphene in aqueous electrolyte.

to other synthesis methods of graphene such as chemical vapor deposition, liquid phase exfoliation, mechanical exfoliation method, epitaxy and hummer's method. Due to large surface area of colloidal dispersion of graphene, it has been suitably utilized for the preparation of flexible energy storage devices [12–15].

4. Electrochemical exfoliation

The colloidal graphene has high specific surface area and does not exhibit aggregation. The colloidal graphene was produced by the intercalation of the sulfate ions in between the individual graphene nanosheets present in the graphite rod. This intercalation process separates the individual graphene nanosheets which accumulate in the electrolyte solution at the end of electrochemical exfoliation process to form the colloidal solution of graphene [14]. Various steps involved in the formation of colloidal solution of graphene through electrochemical exfoliation process are shown in **Figure 2**.

The quality of colloidal graphene produced by the electrochemical exfoliation depends upon the type of the aqueous electrolyte used. Therefore, to improve the quality of colloidal graphene various electrolytes have been studied by researchers [8]. Some of the electrolytes used to prepare colloidal solution of graphene are ammonium sulfate, phosphoric acid, potassium sulfate, sodium sulfate, sulfuric acid electrolytes. In addition of these aqueous electrolytes lithium sulfate has also been observed to produce colloidal solution of graphene via electrochemical route [16].

The electrochemical exfoliation of graphene is performed by using one graphite rod and one platinum wire immersed in any aqueous solution containing sulfate ions. A DC voltage source is used for the exfoliation process [8]. Usually, a DC voltage of 10 V is applied for 1 to 1.5 hour for the exfoliation of graphene to complete. After 1.5 hour, the colloidal solution of graphene is obtained in the aqueous electrolyte solution (**Figure 3**). When the exfoliation process is completed, the graphite rod has been completely converted into graphene colloids in the solution. Later, the colloidal solution of graphene is used for the preparation of the graphene based electrodes.

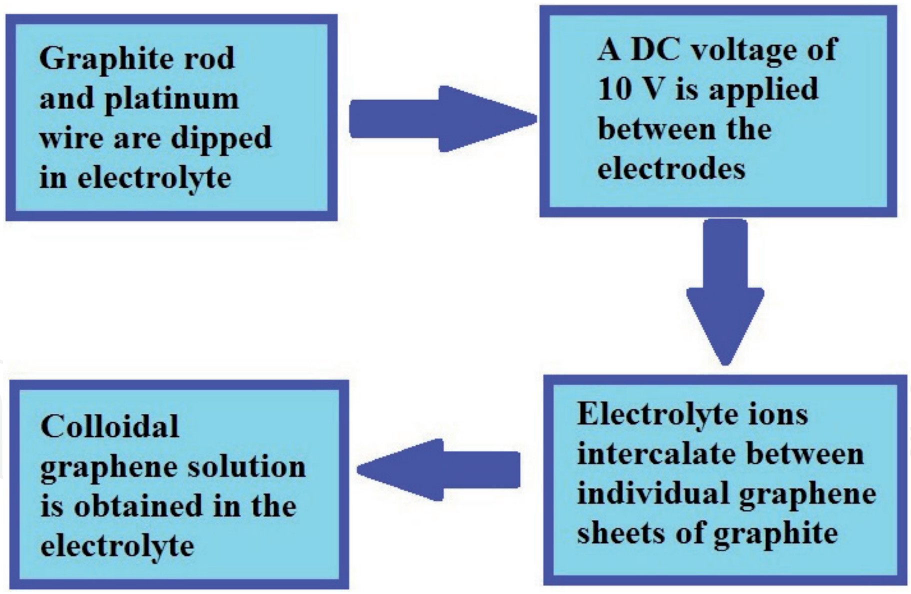

Figure 2.
Various steps involved in the formation of colloidal solution of graphene through electrochemical exfoliation process.

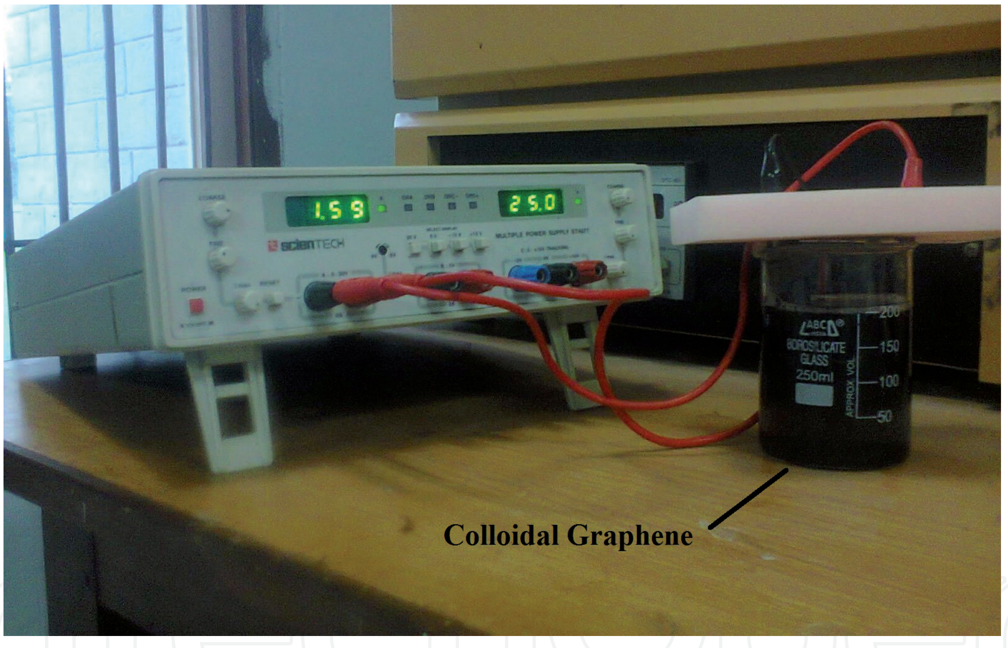

Figure 3.
Electrochemical exfoliation of graphite for the formation of colloidal graphene.

5. Recent works on electrochemical exfoliation of graphene

Due to the various advantages of the electrochemical exfoliation technique in comparison to others, it has been extensively utilized recently for the preparation of graphene nanosheets for various applications. Recently industrial scale synthesis of few-layer graphene nanosheets have been synthesized where the electrochemical experiment shows that rate of graphene exfoliation increases with the higher concentration of intercalates and accordingly the colloidal conductivity changes [17]. In comparison to graphene, graphene oxide is more environment friendly because of the presence of oxygen-containing functional groups. In Comparison to standard Hummers' method for synthesis of GO, electrochemical exfoliation of graphite is considered facile and green with better crystallinity and higher oxidation degree [18].

The role of electrolytes is very important in the quality of the graphene produced. The graphene synthesis mechanism in acidic (0.5 M H_2SO_4), neutral (0.5 M Li_2SO_4) is compared to non-destructive intercalation in organic electrolyte (1 M $NaClO_4$ in acetonitrile) [19]. Another important advantage of electrochemical exfoliation is that it can be utilized for the synthesis of graphene from electronic waste because it is a great threat to the environment due to difficulty in recycling, difficulty in conversion of waste to useful materials. So, researchers have reported a facile and fast production method of electrochemical exfoliation of graphene from graphite of used Zn–C batteries [20]. The quality of graphene produced by the electrochemical exfoliation can be enhanced by taking mixtures of various electrolytes with pencil rods as electrodes. For the synthesis of graphene sheets, different mixtures of H_2SO_4 and HNO_3 solution were investigated with different volume ratios of H_2SO_4: HNO_3, with maximum oxidation was achieved at 1:1 ratio of both mixtures [21]. In another study, electrochemical exfoliation method was used for the preparation of high-quality water-dispersible graphene using molybdate aqueous solutions as the electrolyte [22]. Further, graphene is very effective against the cancer cells for treatment of cancer patients. Some researchers have demonstrated the cytotoxic effect of graphene with high content of nitrogen on colon cancer cells and antioxidant and protective properties on human endothelial cells [23]. Further, the researchers have investigated the role of Transition Metal Salts During Electrochemical Exfoliation of Graphite for Energy Storage Applications [24]. Recently, colloidal graphene produced by the electrochemical exfoliation of graphite in potassium sulphate and sulfuric acid electrolytes has been successfully utilized for the supercapacitor applications [25, 26]. **Table 2** shows various electrolytes used recently for the electrochemical exfoliation of graphene.

S.No.	Aqueous electrolyte	DC Voltage	Concentration	Graphene /GO Exfoliation	Reference
1	Sulfuric Acid	10 V, 3 V	0.5 M to 2 M	Yes	[17]
2	Sodium sulfate, oxalate acid	10 V, 15 V	0.05 M, 0.1 M	Yes	[18]
3	Sulfuric acid, Lithium sulphate	3 V, 5V	0.5 M, 0.5 M	Yes	[19]
4	poly(sodium 4-styrenesulfonate) (PSS)	5 V	0.5 M	Yes	[20]
5	Mixture of Nitric acid and Sulfuric Acid	10 V	0.6 M	Yes	[21]
6	molybdate aqueous solution	9 V, 10 V	0.1 M	Yes	[22]
7	Ammonium sulphate	9 V	0.1 M	Yes	[23]
8	Cobalt sulphate and Sodium sulphate	2 V	0.5 M, 0.05 M	Yes	[24]
9	Potassium Sulphate	10 V	0.1 M	Yes	[25]
10	Sulfuric acid	10 V	0.1 M	Yes	[26]
11	Ammonium sulphate	10 V	0.1 M	Yes	[8]
12	Sodium sulphate	10 V	0.1 M	Yes	[8]
13	Potassium sulphate	10 V	0.1 M	Yes	[8]
14	Ammonium chloride	10 V	0.1 M	NO	[8]

S.No.	Aqueous electrolyte	DC Voltage	Concentration	Graphene /GO Exfoliation	Reference
15	Sodium nitrate	10 V	0.1 M	POOR	[8]
16	Sodium perchlorate	10 V	0.1 M	NO	[8]
17	sodium dodecyl sulphate (SDS)	5 V	0.001 M to 0.1 M	Yes	[27]
18	Sodium Dodecyl Sulphate (SDS)	5 V to 9V	0.1 M to 0.01 M	Yes	[28]
19	TBA·H_2SO_4, NaOH	10 V	0.1 M	Yes	[29]
20	$(NH_4)_2SO_4$,CH_4N_2S	10 V	0.1 M	Yes	[30]
21	sodium saccharin	2 V to 10 V	0.1 M	Yes	[31]
22	NaCl (NaBr,NaI)	10 V	0.05 M	Yes	[32]
23	ionic liquids in acetonitrile	10 V-20 V	0.1 M	Yes	[33]

Table 2.
Recent electrolytes used for the electrochemical exfoliation of graphene.

6. Application of colloidal graphene

The colloidal dispersion of graphene produced by the electrochemical exfoliation method is ideal for the preparation of the graphene based flexible paper electrodes. For this, colloidal graphene is coated using brush coating method on A4 paper and dried. These graphene based flexible paper electrodes are used for the preparation of the flexible energy storage devices [8]. First a gel electrolyte is prepared by using PVA (polyvinyl alcohol) and water [34], then two graphene based paper electrodes are joined using this gel electrolyte in between electrodes. Later, two aluminum foils are joined to form the contacts with these electrodes for taking various measurements of these flexible energy storage devices (**Figure 4**). The actual fabricated flexible energy storage device using colloidal graphene is shown in **Figure 5**.

The performance of the flexible energy storage devices is measured by the CV Curves [8]. Further, the type of the gel electrolyte changes the shape of the CV curve measured and hence the performance of the energy storage device.

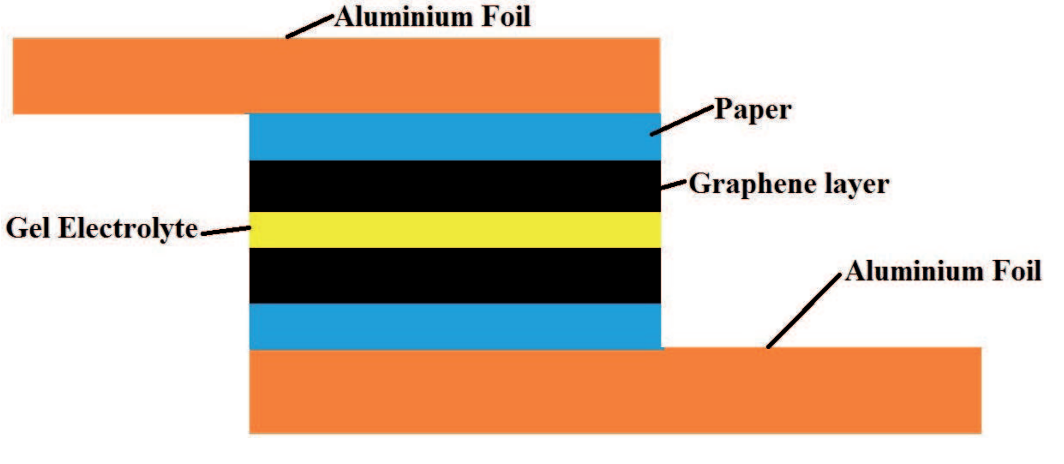

Figure 4.
Schematic diagram of the graphene based flexible energy storage device structure.

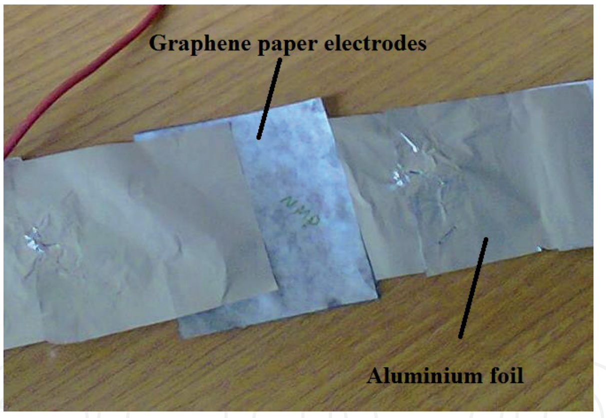

Figure 5.
The flexible energy storage device fabricated using colloidal graphene.

Different flexible energy storage devices can be prepared by using various gel electrolytes and their performance can be compared to obtain the most suitable gel electrolyte for the preparation of the flexible energy storage devices.

7. Conclusion

This review article discusses electrochemical synthesis of colloidal graphene. Colloidal form of graphene is better than other forms of graphene available because of its solution route is easy to be used for the formation of graphene based electrodes. It is observed that electrochemical exfoliation of graphite is the simple, time saving and economical method for the production of colloidal form of graphene. Various aqueous electrolytes can be used for the electrochemical exfoliation of graphene from graphite. After the colloidal solution is obtained it is used for the preparation of the flexible paper electrodes which are suitable for the formation of flexible energy storage devices.

Conflict of interests

The authors declare no conflict of interests.

Author details

Randhir Singh
Department of Electronics and Communication Engineering, University Institute of Engineering and Technology, Kurukshetra University, Haryana, India

Address all correspondence to: mr_randhir_singh@yahoo.co.in

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V & Firosov A A. Electric field effect in atomically thin carbon films. Science. 2004; 306: 666-669.

[2] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V & Geim A K. Two-dimensional atomic crystals. Proc Natl Acad Sci USA. 2005; 30:10451-10453.

[3] Bolotin K I, Sikes K J, Jiang Z, Klima M, Fudenberg G, Hone J, Kim P & Stormer H L. Ultrahigh electron mobility in suspended graphene. Solid State Commun. 2008;146:351-355.

[4] Lee C, Wei X, Kysar J W & Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science. 2008; 321: 385-388.

[5] Zhu Y, Murali S, Cai W, Li X, Suk J W, Potts J R & Ruoff R S. Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater. 2010; 35: 3906-3924.

[6] Moser J, Barreiro A & Bachtold A, Current-induced cleaning of graphene. Appl Phys Lett. 2007; 91: 163513.

[7] Geim, A K & Novoselov, K S, The rise of graphene. Nature Mater. 2007; 6: 183-191.

[8] Khaled Parvez, Zhong-Shuai Wu, Rongjin Li, Xianjie Liu, Robert Graf, Xinliang Feng,Klaus Müllen. Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts. Journal of the American Chemical Society; 2014;136:6083-6091

[9] Zhang Y,Zhang L, Zhou C, Review of Chemical Vapor Deposition of Graphene and Related Applications. Acc. Chem. Res.; 2013; 46: 2329-2339.

[10] Mishra N, Boeckl J, Motta N, Iacopi F. Graphene growth on silicon carbide: A review. Phys. Status Solidi ;2016; 2013: 2277-2289.

[11] Hernandez Y, Nicolosi V, Lotya M, Blighe F.M, Sun Z, De S, McGovern I.T, Holland B, Byrne M, Gun'Ko Y.K, High- yield production of graphene by liquid-phase exfoliation of graphite. Nat. Nanotechnol; 2008; 3: 563-568.

[12] K. Chen, D. Xue, Ionic Supercapacitor Electrode Materials: A System-Level Design of Electrode and Electrolyte for Transforming Ions into Colloids. Colloids Interface Sci. Commun. 2014: 1: 39-42.

[13] K. Chen, D. Xue, $YbCl_3$ electrode in alkaline aqueous electrolyte with high pseudocapacitance. J. Colloid Interface Sci. 2014; 424: 84-89.

[14] K. Chen, D. Xue, Preparation of colloidal graphene in quantity by electrochemical exfoliation. J. Colloid Interface Sci. 2014; 436: 41-46.

[15] K. Chen, D. Xue. Formation of electroactive colloids via in situ coprecipitation under electric field: erbium chloride alkaline aqueous pseudocapacitor. J. Colloid Interface Sci. 2014;430:265-271.

[16] R. Singh. Synthesis of colloidal graphene by electrochemical exfoliation of graphite in Lithium Sulphate. Materials Today Proceedings. 2018 ;5: 973-979.

[17] S. K. Sahoo, A.K. Behera, R. Chandran, A. Mallik. Industrial scale synthesis of few-layer graphene nanosheets (FLGNSs): an exploration of electrochemical exfoliation approach. Journal of Applied Electrochemistry. 2020;6: 673-688.

[18] Duhong Chen, Zhen Lin, Matthew M Sartin, Teng-Xiang Huang, Jia Liu, Qiugen Zhang, Lianhuan Han, Jian-Feng

Li, Zhong-Qun Tian, Dongping Zhan. Photosynergetic Electrochemical Synthesis of Graphene Oxide. J Am Chem Soc. 2020 ;142:6516-6520.

[19] Zhenyuan Xia, Vittorio Bellani, Jinhua Sun, Vicenzo Palermo. Electrochemical exfoliation of graphite in H_2SO_4, Li_2SO_4 and $NaClO_4$ solutions monitored in-situ by Raman microscopy and spectroscopy. Faraday Discussions. 2020.

[20] Bagas Prakoso, Yuanyuan Ma, Ruth Stephanie, Naufal Hanif Hawari, Veinardi Suendo, Hermawan Judawisastra, Yun Zong, Zhaolin Liu, Afriyanti Sumboja. Facile synthesis of battery waste-derived graphene for transparent and conductive film application by an electrochemical exfoliation method. RSC Adv. 2020; 10: 10322-10328.

[21] Hamed Aghamohammadi, Reza Eslami-Farsani. An experimental investigation on the sulfur and nitrogen co-doping and oxidation of prepared graphene by electrochemical exfoliation of pencil graphite rods. Ceramics International. 2020;46: 28860-28869.

[22] Juan Wu; Hongfei Wang; Jun Qiu; Jingwen Shao; Kefu Zhang; Lifeng Yan. Electrochemical exfoliation for few-layer graphene in molybdate aqueous solution and its application for fast electrothermal film. Progress in Natural Science: Materials International. 2020; 30:312-320.

[23] Ioana Baldea, Diana Olteanu, Gabriela Adriana Filip, Florina Pogacean, Maria Coros, Maria Suciu, Septimiu Cassian Tripon, Mihai Cenariu, Lidia Magerusan, Raluca-Ioana Stefan-van Staden, Stela Pruneanu. Cytotoxicity mechanisms of nitrogen-doped graphene obtained by electrochemical exfoliation of graphite rods, on human endothelial and colon cancer cells. Carbon; 2019;158:267-281.

[24] Andinet Ejigu, Kazunori Fujisawa, Ben F. Spencer, Bin Wang, Mauricio Terrones, Ian A. Kinloch, Robert A. W. Dryfe. Electrochemical Exfoliation: On the Role of Transition Metal Salts During Electrochemical Exfoliation of Graphite: Antioxidants or Metal Oxide Decorators for Energy Storage Applications. Advanced Functional Materials: 2018; 28:1804357.

[25] Singh R. Electrochemical Exfoliation of Graphite into Graphene for Flexible Supercapacitor Application. Materials Today Proceedings. 2018;5:1125-1130

[26] Singh R. Study of Graphene based Flexible Supercapacitors with Different Gel Electrolytes Materials Today Proceedings. 2018;5:943-949

[27] Nurhafizah Md Disa, Suriani Abu Bakar, Suhufa Alfarisa, Azmi Mohamed, Illyas Md, AzlaN Kamari, Norhayati Hashim, Azira Abd. Aziz,Mohamad Rusop Mahmood. The Synthesis of Graphene Oxide via Electrochemical Exfoliation Method. Advanced materials research;2015;1109:55-59

[28] Wan Hazman Danial, Arunabhiram Chutia, Zaiton Abdul Majid, Riadh Sahnoun, Madzlan Aziz. Electrochemical Synthesis and Characterization of Stable colloidal Suspension of Graphene using Two-electrode Cell System. AIP Conference Proceedings;2015; 1669: 020020.

[29] Yang S, Ricciardulli AG, Liu S, et al. Ultrafast delamination of graphite into high-quality graphene using alternating currents. Angew Chem. 2017;56:6669-6675.

[30] Li L, Wang M, Guo J, et al. Regulation of radicals from electrochemical exfoliation of a double-graphite electrode to fabricate high-quality graphene. J Mater Chem C. 2018;6:6257-6263.

[31] Kumar MK P, Shanthini S, Srivastava C. Electrochemical exfoliation

of graphite for producing graphene using saccharin. RSC Adv. 2015;5:53865-53869.

[32] Munuera JM, Paredes JI, Enterría M. Electrochemical exfoliation of graphite in aqueous sodium halide electrolytes toward low oxygen content graphene for energy and environmental applications. ACS Appl Mater Interfaces; 2017; 9:24085-24099.

[33] Taheri Najafabadi A, Gyenge E. Synergistic production of graphene microsheets by simultaneous anodic and cathodic electro-exfoliation of graphitic electrodes in aprotic ionic liquids. Carbon; 2015;84:449-459.

[34] Farshad Barzegar, Julien K. Dangbegnon, Abdulhakeem Bello, Damilola Y. Momodu. Effect of conductive additives to gel electrolytes on activated carbon-based supercapacitors. AIP Advances.2015;5:97171-97179